

1078,400

PATENT SPECIFICATION

NO DRAWINGS

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Inventor: BALACHANDRA CHAKKINGAL SEK HAR

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COMPLETE SPECIFICATION

Processing Improvements to Synthetic Rubbers

- We, THE BOARD OF THE RUBBER RESEARCH INSTITUTE OF MALAYA, a body corporate having perpetual succession and a common seal and who may sue and be sued in all courts by the name of "The Board of the Rubber Research Institute of Malaya" of 3rd Mile Ampang Road, Kuala Lumpur, Malaya, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
- This invention relates to the manufacture of synthetic rubbers or blends of synthetic rubbers with natural rubbers having improved processing properties.
- In British Patent Specification Nos. 803,013 and 880,739, methods are described for improving the processing properties of rubbers. In the former specification, natural rubber in sheet or crepe form having improved processing properties is prepared by adding a proportion of vulcanised natural rubber latex to an unvulcanised natural rubber latex and coagulating the mixture of latices. The latter patent specification describes a process in which a masterbatch is first formed by incorporating a high proportion of vulcanised natural rubber latex into unvulcanised natural rubber latex and the masterbatch so obtained is, after coagulation, mixed with unvulcanised natural or synthetic rubbers to provide rubbers having improved processing properties.
- We have now found that the processing properties of both natural and synthetic rubbers are improved by mixing a synthetic rubber latex which has been vulcanised to a certain sulphur content with an unvulcanised natural and/or synthetic rubber latex and either using the coagulated mixed latex directly in the manufacture of rubber articles or using it as a masterbatch for blending with unvulcanised natural and/or synthetic rubber to improve the processing properties thereof.
- In the synthetic rubber industry it is common practice to mix a synthetic rubber, which has been cross-linked with divinyl benzene, with unvulcanised synthetic rubber in order to improve its processing properties. We have established, however, that the incorporation of a synthetic rubber masterbatch prepared in accordance with the present invention into an unvulcanised synthetic rubber produces a greater improvement in the processing properties of the rubber than is obtainable by using a divinyl benzene-cross-linked rubber as a processing aid.
- According to the present invention there is provided a process for the preparation of synthetic rubbers or blends of synthetic rubbers with natural rubber having improved processing characteristics which comprises mixing a synthetic rubber latex, which has been vulcanised to a sulphur content of from 1 to 2.5% by weight of the latex solids, with an unvulcanised sulphur-vulcanisable synthetic and/or natural rubber latex in an amount such that the resulting mixture of latices contains from 5 to 95% by weight of the vulcanised rubber based on the solids contents of the latices and thereafter coagulating the mixture of latices.
- The synthetic rubbers which are sulphur-vulcanisable are those which are produced by polymerisation of diene monomers, either alone or with other unsaturated monomers, examples of suitable rubbers being styrene/butadiene, polybutadiene, cis-polyisoprene and butadiene/acrylonitrile rubbers.
- Where the mixture of latices contains from 5 to 50% of the vulcanised component, the rubber may be used directly in the production of rubber articles. In cases where the mixture of latices contains more than 50% of the vulcanised component, the rubber may be used as a masterbatch and mixed with additional unvulcanised natural and/or synthetic rubber to impart thereto the desired degree of im-

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5 improvement in processing characteristics. We have found that the addition of the masterbatch to natural and/or synthetic rubber in amounts such that the proportion of vulcanised rubber constitutes from 15 to 20% by weight of the final blend improves substantially the processing characteristics of the rubber during milling, calendaring and extrusion.

10 If desired, the vulcanised synthetic rubber latex may be partly replaced with vulcanised natural rubber latex, preferably in a minor amount, and the mixture of vulcanised latices mixed with the unvulcanised synthetic and/or natural rubber latex in an amount such that the resulting mixture of latices contains from 5 to 95% by weight of the mixture of vulcanised latices based on the solids contents of the latices.

20 In the following examples, which are given to illustrate the invention and the manner of carrying it into effect, all parts and percentages are by weight unless otherwise expressly stated to the contrary and the abbreviations "RSS" and "SBR" mean natural rubber ribbed smoked sheet and a styrene/butadiene rubber, respectively.

Example 1

30 To 1,000 gms. of SBR latex containing 600 gms. of rubber solids, the following additions were made:—

(i) Sufficient ammonia to increase the pH to a value greater than 10.

35 (ii) An aqueous dispersion containing 12 gms. of sulphur, 2.4 gms. of mercaptobenzthiazole, 1.2 gms. of zinc diethyl dithiocarbamate, and 4.5 gms. of zinc oxide.

The latex mixture is then heated with stirring at a temperature of 85 — 90°C. for 1½ hours to effect vulcanisation of the rubber.

40 The resulting vulcanised latex was then mixed with the original unvulcanised SBR latex in the ratios of (1) 1:4 and (2) 4:1 by weight based on rubber solids contents. A sample (3) of the original unvulcanised SBR latex was used as a control. All three samples were coagulated using formic acid and the coagula were creped. The following observations were made:—

Sample (1) No difficulty in crepeing into a form thin enough to dry

Sample (2) No difficulty at all in crepeing and a very thin crepe can be produced.

Sample (3) Great difficulty in crepeing and the crepe was too thick for normal drying.

55 Samples (1) and (3) after drying were compounded using the following tread mix recipe and then extruded; rubber 100.00, Philblack 0 (High abrasive furnace black) 50.00, zinc oxide 5.00, stearic acid 4.00, Santocure (cyclohexyl benzthiazyl sulphenamide) 0.60, pine tar 3.00 and sulphur 2.50 parts. (PHILBLACK and SANTOCURE are Registered Trade Marks.) A portion of the masterbatch sample (2) was mixed with the following rubbers; (a) RSS, (b) oil-extended SBR and (c) SBR, the proportion of masterbatch to the other rubber being in each case 1:3. The resulting 3 rubber compositions designated as 2(a), 2(b) and 2(c), and samples of the 3 rubbers used for blending with the masterbatch, designated as (a), (b) and (c), were compounded with the above tread-mix recipe and extruded. Observations were made of the extrusion of the compounded rubbers and also the extrusion of samples (1) and (3) above and the results of the extrusion swell test described below are given in the following Table.

TABLE I

Sample	Nature of Extruded Surface	% Extrusion Swell
(1) Creped SBR latex containing 20% vulcanised SBR	Smooth	16.5
2(a) Masterbatch + RSS	Very smooth	8.5
2(b) Masterbatch + oil-extended SBR	Very smooth	13.0
2(c) Masterbatch + SBR	Very smooth	15.4
Controls		
(3) Creped unvulcanised SBR latex	Excessively rough	Surface too rough to measure swell
(a) RSS	Smooth	17.5
(b) Oil-extended SBR	Smooth	21.5
(c) SBR	Smooth	27.1

5 The extrusion swell test was carried out as follows: 200 gms of the rubber after crepe-
 10 ing and drying were taken and compounded with 100 gms of Philblack 0 (High abrasive furnace black), 10 gms of zinc oxide, 8 gms
 15 of stearic acid, 1.2 gms of Santocure (cyclohexyl benzthiazyl sulphenamide), 6 gms of pine tar and 5 gms of sulphur. The compound-
 20 ed rubber was then raised to a temperature of 100°C. and extruded through an orifice of known dimensions. The extruded rod was allowed to cool and its cross-sectional area was calculated from weight and density measurements of a particular length of the rod. The difference between the cross-sectional area of the rod and that of the orifice gives a measure of the extrusion swell of the rubber. The extrusion swell test is a standard method of comparing the processing characteristics of rubbers and the smaller the figure for the per-

centage extrusion swell of a particular rubber, the better are its processing properties.

25 A comparison was then made of the effect of sample (2) of SBR masterbatch rubber as a processing aid for Krylene NS rubber, which is a low temperature SBR, with that of SX 371 (a divinyl benzene cross-linked SBR) as a processing aid for the same rubber (KRYLENE is a Registered Trade Mark). The untreated Krylene NS rubber and mixtures of this rubber with the two processing aids were subjected to the extrusion swell test described above and the results are given in Table II below. The processing aid SX 371 was mixed with the Krylene NS rubber in the ratio of 1:4 by weight, while the SBR masterbatch was mixed with the Krylene NS rubber in the ratio of 1:3 by weight, so that the resulting mixture in both cases contained 20% by weight of cross-linked rubber. 40

TABLE II

Sample	% Extrusion Swell
Krylene NS	27.1
SX—371 + Krylene NS	20.2
SBR (2) Masterbatch + Krylene NS	15.4

For any processing aid to be successful, the physical properties of the final blend containing the processing aid should also be satisfactory. Table III, therefore, shows the physical properties of a sample of compounded Krylene

NS rubber which has been processed with the SBR (2) masterbatch and these are compared with the properties of untreated Krylene NS rubber. The mix used is as follows:—

	SBR (Krylene NS)	SBR + SBR (2) Masterbatch
SBR (2) Masterbatch	—	25.00
Krylene NS	100.00 parts	75.00 parts
Santocure	1.2 „	1.2 „
zinc oxide	3.5 „	3.5 „
stearic acid	2.0 „	2.0 „
Santoflex DPA	1.5 „	1.5 „
sulphur	1.8 „	1.8 „
High abrasive furnace black	50.0 „	50.0 „
Circosol 2XH	6.0 „	6.0 „

Santoflex DPA is a Registered Trade Mark for a diphenylamine-acetone blend while Circosol 2XH is a trade name for a naphthenic oil.

TABLE III

Sample	Tensile Strength kgms/cm ²	Modulus 300% kgms/cm ²	Extension at break %	Resilience %	Hardness °BSI
SBR (Krylene NS)	227	149	442	59	67.9
SBR + SBR (2) Masterbatch	197	185	330	61	75.0

Thus it can be seen that a compounded rubber which has been processed with the aid of SBR masterbatch has physical properties which compare favourably with those of a compounded rubber which has not been processed with a processing aid.

EXAMPLE II

A sample of a latex produced from butadiene and acrylonitrile and sold under the Registered Trade Mark "Hycar" was subjected to vulcanisation in latex form by heating for 2 hours at 85° — 90°C. using a vulcanising mixture consisting of 2% sulphur, 0.75% zinc oxide, 0.4% mercaptobenzthiazole and 0.2%

zinc diethyl dithiocarbamate. The resulting latex was then mixed with unvulcanised "Hycar" latex in the ratio of 4:1 by weight based on rubber solids contents. The mixture was then coagulated with formic acid and the crumb dried. The dried crumb was mixed on the mill with (a) raw natural rubber (b) three samples of the butadiene/acrylonitrile rubbers sold under the Registered Trade Mark "Polysar Krynac" 800, 802 and 803, compounded in a tread mix recipe and subjected to the extrusion test described in Example 1. Table IV below gives results of the extrusion swell tests.

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TABLE IV

Rubber	Type	Mooney Viscosity	% Extrusion Swell	
			Rubber	Rubber + Masterbatch
Natural rubber	—	75	15.5	6.4
Polysar Krynac 800	66% butadiene 34% acrylonitrile	83	46.9	23.7
Polysar Krynac 802	73% butadiene 27% acrylonitrile	83	40.0	22.9
Polysar Krynac 803	66% butadiene 34% acrylonitrile	47	44.3	19.2

WHAT WE CLAIM IS:—

1. A process for the preparation of synthetic rubbers or blends of synthetic rubbers with natural rubbers having improved processing characteristics which comprises mixing a synthetic rubber latex, which has been vulcanised to a sulphur content of from 1 to 2.5% by weight of the latex solids, with an unvulcanised sulphur-vulcanisable synthetic and/or natural rubber latex in an amount such that the resulting mixture of latices contains from 5 to 95% by weight of vulcanised rubber based on the solids content of the latices and thereafter coagulating the mixture of latices.
2. A process according to claim 1 wherein the mixture of latices is coagulated by addition of formic acid thereto.
3. A process according to claim 1 or claim 2 wherein the vulcanised synthetic rubber latex is replaced in part with vulcanised natural rubber latex.
4. A process according to any of the preceding claims wherein the coagulated mixture of latices contains from 50 to 95% of vulcanised rubber and is used as a masterbatch by mixing

it with unvulcanised synthetic and/or natural rubber to produce a final rubber blend having improved processing characteristics.

5. A process according to claim 4 wherein the mixture of latices is mixed with the unvulcanised synthetic and/or natural rubber in amounts such that the proportion of vulcanised rubber constitutes from 15 to 20% by weight of the final blend.

6. A process for the preparation of synthetic rubbers or blends of synthetic rubbers with natural rubbers having improved processing characteristics as claimed in claim 1 and substantially as described with reference to the Examples.

7. Synthetic rubbers and blends of synthetic rubbers with natural rubbers having improved processing characteristics when prepared by the process claimed in any of the preceding claims.

STEVENS, LANGNER, PARRY &
ROLLINSON,
Chartered Patent Agents,
Agents for the Applicants.

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